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PATENT SPECIFICATION.

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(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1942, became operative on May 15, 1945).

COMPLETE SPECIFICATION

New Synthetic Drying Oils and Coating Compositions.

We, E. I. Du Pont de Nemours and Co., a corporation existing under the laws of the State of Delaware, located at Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new synthetic drying oils and to coating compositions containing them.

The higher grade natural drying oils, such as China wood, perilla and oiticica oils, are for the most part imported and are subject to wide fluctuation in price, quality, and availability. Some of these oils have a tendency to form films which "crystallize" or "frost". Previous attempts to provide synthetic substitutes having the desirable film-forming characteristics of these natural oils have been for the most part unsatisfactory in one or more ways.

This invention accordingly has as its general objective the preparation of new esters which can be substituted for the rapidly drying natural fatty oils in coating compositions into which fatty oils are ordinarily formulated.

According to the invention we manufacture, by the processes hereinafter set forth, glycerol ester of one or more acrylic/monofunctional monocarboxylic acids as hereinafter defined, and, if desired, one or more monofunctional aliphatic monocarboxylic acids of different structure. Thus the glycerol esters may be simple esters (i.e. all the hydroxyls of the glycerol being esterified with one and the same acylacrylic acid) or they may be mixed esters, in which the hydroxyls of the glycerol are esterified with different acylacrylic acids or with an acylacrylic acid and one or more other monofunctional aliphatic monocarboxylic acids of different structure. The latter acids are preferably unsaturated, the acids of natural drying or semi-drying oils being most useful. The mixed esters can also be designated as glycerol mixed esters, the acyl radicals of which comprise those of the acylacrylic acid and a monofunctional aliphatic monocarboxylic acid of different structure.

The expression "acylacrylic acid" is used in a generic sense to designate any of those keto-monocarboxylic acids having an ethylenic double bond between the α and β carbon atoms and an acyl group attached to either the α or β carbon. The novel properties of the products of the invention are considered to depend from this particular and peculiar arrangement of carboxyl group, ethylenic double bond, and ketone group. The remainder of the molecule is substantially immaterial provided the acid is "monofunctional", i.e., contains no groups, for example hydroxyl, primary amino, secondary amino or sulphydryl groups which are known to react with the carboxyl group under normal esterification conditions and there be no aryl group attached to the β carbon atom and no thienyl group attached to the α or β carbon atoms.

The simple esters referred to above can be prepared by reacting glycerol with the acylacrylic acid or appropriate esterifiable derivative thereof, such as an acid halide or an ester with an alcohol more volatile than glycerol. The mixed esters can be prepared in general by reacting the glycerol, simultaneously or successively, in either order, with the several monocarboxylic acids or their esterifiable derivatives, such acids including at least one acylacrylic acid and, usually, at least one monofunctional aliphatic monocarboxylic acid of different structure. It is to be noted, however, that the α-acylacrylic acids are in general relatively unstable as free acids, and their glycerol esters, simple or mixed, are best prepared by ester interchange from an ester of the α-acylacrylic acid with an alcohol more volatile than glycerol.

In one method of preparing the mixed esters, the acylacrylic acid, or ester thereof with an alcohol more volatile than

glycerol, is reacted with glycerol which has been partially esterified with a different monofunctional aliphatic monocarboxylic acid or acids. These glycerol partial esters are most suitably obtained by heating fatty oils in the usual way with glycerol and, preferably, an ester interchange catalyst. In carrying out this alcoholysis step, the oil and free glycerol, in proportions calculated to give the degree of alcoholysis desired, are placed, along with a small amount of alcoholysis catalyst (e.g., 0.01 to 0.1% litharge based on the oil), in a reactor fitted with an agitator, a device to measure the temperature, and a gas inlet. The mixture is then heated with stirring for 1 to 2 hours at about 200—250° C., an oxygen-free inert gas such as carbon dioxide or nitrogen being passed into and over the mixture. In the esterification step, this glycerol partial ester is usually cooled to about 140—150° C., and the acylacrylic acid, or esterifiable derivative, is introduced in approximately the amount sufficient to esterify the free hydroxyl groups calculated to be present from the initial proportions of oil and glycerol. A hydrocarbon solvent, such as xylene or toluene, is next added in an amount sufficient to produce boiling when the temperature reaches about 200° C. The distilling vapours of solvent and water of esterification are passed through a downward condenser, the water is separated mechanically from the condensed liquids, and the solvent returned to the reaction vessel, the whole cycle of distillation, separation of water, and return of solvent being conducted in a continuous manner. Depending on the temperature of reaction, which in turn is governed by the nature and amount of solvent employed, the reaction is usually completed within 4—16 hours; thus, when the temperature is about 200° C., the process is usually completed within 4—10 hours. The reaction can be accelerated if desired by means of esterification catalysts, such as sodium bisulphate. The progress of the reaction can be followed by acid number determinations, the heating being stopped when the acid number reaches or approaches constancy, or at any desired value. There is obtained a viscous solution of the new glycerol ester from which the solvent can be removed, if desired, by distillation or by forcing a rapid stream of carbon dioxide through the mixture. This ester can be formulated, by conventional methods used with natural drying oils, into valuable coating compositions. For such purposes, it can be used alone, or in blends with natural or synthetic resins and/or natural drying or semi-drying oils. Hot blending of these new esters with the natural drying or semi-drying oils gives coating composition vehicles of unique properties.

In preparing the esters of the present invention, certain precautions are often necessary in order to obtain satisfactory results from a number of standpoints.

The esterification reaction for the preparation of the drying oil is preferably carried out at as low a temperature as is practical. Another such precaution is the maintenance of an inert atmosphere by the use of an oxygen-free inert gas. By complete or essentially complete exclusion of oxygen, superior colour is obtained, while, if the reaction is carried out at high temperature in the presence of oxygen, poorer colour, combined with decomposition and sometimes inferior drying, is encountered. To obtain light-coloured products, it is also necessary to avoid use of materials which liberate oxygen under reaction conditions. Thus, solvents employed should not be those which contain or give off free oxygen or similar active products during the reaction. For example, aged turpentine or old samples of petroleum naphtha should not be used since the peroxides usually present in these materials produce deleterious effects. Other oxygen-yielding compounds, for example, oxidized drying oils, should be excluded in order to insure good colour, and to avoid degradation and gelation of the resulting compositions.

The more detailed practice of the invention is illustrated but not limited by the following examples wherein the parts are by weight. In these examples, viscosities and colours are given on the Gardner-Holdt scale, and the hydroxyl numbers are all corrected for acidity. Where the use of cobalt drier is mentioned, sufficient of a 2% cobalt naphthenate solution has been used to give the indicated content of cobalt metal, this proportion being based on oil.

The ester compositions in the title of each example do not mean that the product actually contains the stated percentages of triglycerides, but are instead an index to the proportion of monoacarboxylic acid radicals in the product.

To illustrate, a product referred to as having 24.4% β-benzoylacrylic acid glyceride and 75.6% linseed acids glyceride is a product prepared from proportions of reactants so chosen as to yield theoretically a mixture of the two mentioned glycerides in the stated proportions by weight, i.e., if it be assumed no mixed ester is formed. Actually, such a product is considered to be composed principally of mixed glycerides, probably

mixtures of mixed glycerides, though small amounts of simple glycerides, partial glycerides (i.e., glycerol incompletely esterified), free glycerol, and free acids are probably present. The significance of the acylacrylic acid ester content is discussed following the examples.

EXAMPLE 1.

GLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND β-BENZOYLACRYLIC ACID.

β-Benzoylacrylic Acid Glyceride – – –	24.4%
Linseed Acids Glyceride –	76.6%

A partial glycerol ester of linseed oil acids, commonly called linseed oil diglyceride, is first prepared by heating 1300 parts of alkali-refined linseed oil and 69.4 parts of refined glycerol for 1.5 hours at 250° C. in an inert atmosphere. To 107 parts of this diglyceride are added 12 parts of toluene and 32 parts of β-benzoylacrylic acid of melting point 94—97° C. (obtainable from benzene and maleic anhydride according to the general method outlined by von Pechmann, Ber., *15*, 885 (1882)), and the solution is refluxed for 9.5 hours at 200—210° C. in an apparatus equipped to allow the condensation of toluene and water of esterification, separation of the water, and return of toluene to the reaction vessel. An inert atmosphere of carbon dioxide is maintained throughout this esterification, and at the completion of the reaction a vigorous current of carbon dioxide is blown through the reaction mixture at 200° C. for 20 minutes in order to remove solvent and traces of unreacted acid. After being cooled and filtered, the resulting oil is found to possess the following physical and analytical values: n_D^{25} 1.5100; hydroxyl no. 20.2; acid no. 1.3. With 0.03% cobalt, this oil dries after 8 hours at room temperature over wood and steel to films which are hard, light-coloured, and tack-free. On baking, for example at 100° C., drying is much faster, and, if desired, driers can be eliminated. Dried films are hard, glossy and adherent, and are similar in many respects to those obtained from China wood oil-limed rosin varnishes or from perilla oil-"Amberol" varnishes of about 45-gallon oil length. Unmodified linseed oil under the same drying conditions is tacky and eventually dries to a soft, weak film having residual tack. Exposures over steel and undercoats after 8 months in Delaware show durability definitely superior to the above varnish controls.

The above product can be made into a varnish as follows: 30 parts of the oil are boiled at 280° C. for 2.25 hours to a thin string. At this point, 7.6 parts of an "Amberol" resin and 0.14 part of lime are added with vigorous stirring. The resulting solution is heated for an additional 0.5 hour at 280° C., cooled to 150° C., and 38 parts of an aromatic hydrocarbon thinner are added. After addition of lead naphthenate and manganese resinate driers, the varnish is filtered. The viscosity of the cooled varnish at 50% solids is G—H. Films of this varnish dry tack-free in 4 hours at room temperature and are light in colour, clear, and after overnight dry are of a hardness similar to that of films from a perilla varnish of comparable oil length.

This oil can also be made into an enamel as follows: 50 parts of the oil, 25 parts of titanium dioxide, 25 parts of antimony oxide, and 20 parts of a hydrocarbon thinner are ground together to give a dispersed system. Cobalt and lead driers in amounts of 0.03% and 0.3%, respectively, are added. This enamel dries in 10—15 hours at 25° C. to films which are tack-free and hard.

EXAMPLE 2.

GLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND β-(2:4-DIMETHYLBENZOYL) ACRYLIC ACID.

β-(2:4-Dimethylbenzoyl) acrylic Acid Glyceride – –	27.0%
Linseed Acids Glyceride – –	73.0%

To 72 parts of the linseed oil diglyceride described in Example 1 are added 25 parts of β-(2:4-dimethylbenzoyl) acrylic acid of melting point 114° C. (prepared from xylene and maleic anhydride by the general method of Hertzowna and Maechelewski, C.Z. 34, 11, 567) and 10 parts of toluene. This mixture is refluxed for 7 hours at 200—210° C. in the type of apparatus described in the previous example. A vigorous stream of carbon dioxide is next blown through the reaction mixture at 200° C. for 20 minutes in order to remove solvent and unreacted acid. After being cooled and filtered, the resulting oil is found to possess the following physical and analytical values: hydroxyl no. 33.3; acid no. 3.68; viscosity Z—4. Thin films of this oil containing 0.03% cobalt drier are dust-free in less than 3 hours at room temperature, and after 8—10 hours are hard and tack-free. Films of this oil are similar to films of the oil described in Example 1.

EXAMPLE 3.

GLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND α-ACETOCROTONIC ACID.

α-Acetocrotonic Acid Glyceride	16.7%
Linseed Acids Glyceride – –	83.3%

To 9.8 parts of refined glycerol is added 30 parts of methyl α-acetocrotonate of boiling point 98—90° C./12 mm. (prepared by condensing acetaldehyde with methyl aceto-acetate in the presence of hydrogen chloride catalyst according to the method of Claisen and Matthews, Ann. *218*, 172 (1883)). This mixture is then heated in the presence of 0.24 part of litharge catalyst for 28 minutes at 181—195° C. in apparatus similar to that described in Example 1. During this time, 6 parts of methanol are evolved, indicating nearly complete ester interchange between methyl α-acetocrotonate and glycerol. After blowing a vigorous current of carbon dioxide through the reaction mixture for 5 minutes to remove traces of methanol, the product is cooled somewhat, and a mixture of 40 parts of linseed oil acids and 118 parts of alkali-refined linseed oil is added. After 12 hours heating at 200—220° C. under conditions described in Example 1, a homogeneous oil having the following physical and analytical values is formed: N_D^{25} 1.4880; hydroxyl no. 13.01; acid no. 6.5; viscosity F; color 6.6. Thin films of this oil containing 0.03% cobalt drier over a steel substrate are hard, light-coloured, and tack-free after air-drying for 10—15 hours at about 25° C. Unmodified linseed oil under the same drying conditions is tacky and eventually dries to a soft, weak film.

EXAMPLE 4.

GLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND α-ACETO-β-(2-FURYL) ACRYLIC ACID.

α-Aceto-β-(2-furyl) acrylic Acid Glyceride – – – –	20.0%
Linseed Acids Glyceride –	80.0%

To 9.8 parts of refined glycerol are added 41 parts of methyl α-aceto-β-(2-furyl) acrylate of boiling point 150—158° C./2 mm. (prepared by condensing furfural and methyl acetoacetate, using piperidine as catalyst, according to the method of Knoevanagel, Ber. *31*, 734 (1898)) and 0.32 part of litharge. This mixture is heated for 25 minutes at 190—200° C. under the conditions of Example 4. To the partial glyceride thus formed are added 48 parts of linseed oil acids and 163 parts of alkali-refined linseed oil, and the resulting mixture is heated for 12 hours at 200—215° C. under the conditions given in Example 1. The resulting homogeneous oil possesses the following physical and analytical values: N_D^{25} 1.4910; hydroxyl no. 18.47; acid no. 7.07; viscosity E. Thin films of this oil containing 0.03% cobalt over a steel substrate dry to exceptionally hard, flexible, adherent, and tack-free films after about 10 hours at room temperature. Such films are strikingly superior to unmodified linseed oil and are also superior in hardness and toughness to films obtained from China wood oil-limed rosin varnishes or from perilla oil-"Amberol" varnishes of about 45-gallon oil length.

EXAMPLE 5.

GLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND 2-ACETO-5-PHENYLPENTADIEN-2:4-OIC ACID.

2-Aceto-5-phenylpentadien-2:4-oic Acid Glyceride – –	20.0%
Linseed Acids Glyceride – –	80.0%

To 5.3 parts of refined glycerol are added 24 parts of methyl 2-aceto-5-phenylpentadien-2,4-oate of boiling point 183—188° C./2 mm. (prepared by condensing cinnamaldehyde and methyl acetoacetate using piperidine catalyst according to the method of Knoevanagel, Ber. *31*, 734 (1899)) and 0.20 part of litharge catalyst. This mixture is heated for 0.5 hour at 186—200° C. under conditions described in previous examples. To the partial glyceride thus formed are added 22.7 parts of linseed oil acids and 95.5 parts of alkali-refined linseed oil, and the mixture is heated at 200—215° C. for 12 hours under conditions described previously. The resulting homogeneous oil is found to possess the following physical and analytical values: N_D^{25} 1.4943; hydroxyl no. 15.97; acid no. 8.30; viscosity E; color 9.0. Thin films of this oil containing 0.03% cobalt over a steel substrate are hard, light-coloured, and tack-free after air-drying for 10—15 hours at about 25° C. Linseed oil under the same drying conditions is tacky and eventually dries to a soft, weak film having residual tack.

EXAMPLE 6.

GLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND α-ACETO-β-(2-FURYL) ACRYLIC ACID.

α-Aceto-β-(2-furyl) acrylic Acid Glyceride – – – –	23.2%
Linseed Acids Glyceride – –	76.8%

To 74 parts of linseed oil diglyceride

prepared as described in Example 1 are added 25 parts of ethyl α-aceto-β-(2-furyl) acrylate and 0.1% of litharge based on the linseed oil diglyceride. This mixture is heated in a carbon dioxide atmosphere with rapid stirring in a vessel fitted with a separatory funnel, agitator, gas inlet tube, and efficient fractionating column. Enough toluene is introduced into the reaction vessel so that refluxing occurs at the head of the fractionating column when the bath temperature is 200—240° C. Under these conditions, a toluene-ethanol binary boiling at 70—104° C. distils off. In this way, the theoretical amount of ethanol (5.5 parts) is collected during 7 hours. After removing toluene and traces of ethanol from the residue, a homogeneous oil having the following physical and analytical values is obtained: N_D^{25} 1.495; hydroxyl no. 64.35; acid no. 24.05. Thin films of this oil containing 0.03% cobalt dried over a steel substrate are hard, flexible, adherent, and tack-free after air-drying for 2—3 days at room temperature.

EXAMPLE 7.

OLYCEROL MIXED ESTER OF LINSEED OIL ACIDS AND β-DIBENZOFUROYLACRYLIC ACID.

β-Dibenzofuroylacrylic Acid Glyceride	32.0%
Linseed Acids Glyceride	68.0%

To 61.6 parts of linseed oil diglyceride described in Example 1 are added 26.6 parts of β-dibenzofuroylacrylic acid and 10 parts of toluene. This mixture is refluxed for 4 hours at 175—183° C., employing 0.1% of sodium bisulphate catalyst based on diglyceride, in the type of apparatus described in Example 1. A vigorous stream of carbon dioxide is next blown through the reaction mixture at 185° C. for 20 minutes to remove solvent. After being cooled and filtered, the resulting oil is found to possess the following physical and analytical values: hydroxyl no. 11.9; acid no. 4.2; viscosity Z—2. Thin films of this oil containing 0.03% cobalt, after drying for 10—15 hours at room temperature, are very hard, tough, and possess good flexibility.

The β-dibenzofuroylacrylic acid referred to above is prepared by stirring a solution of 49 parts of dibenzofurane and 29 parts of maleic anhydride in 190 parts of carbon disulphide with 80 parts of aluminium chloride for 20—30 minutes. No external heat is applied since the heat of reaction is sufficient to keep the carbon disulphide refluxing. The crude acid separates when the reaction mixture is poured into acidified water. It is purified by dissolving it in dilute aqueous sodium carbonate, filtering, and reprecipitating by addition of acid. After washing in water and drying, the acid melts at 205° C., and has a neutralization equivalent of 269, the calculated value being 266. In regard to the glycerol mixed esters of acylacrylic acids generally, and more particularly in regard to glycerol mixed esters of β-benzoylacrylic acid and drying or semi-drying oil acids (especially linseed oil acids), it will usually be found that the products which dry fastest and have best film properties generally have of the order of 10—40% β-acylacrylic acid glyceride. The proportions for best results will, however, vary somewhat with the particular ingredients.

After the film-forming properties of esters obtained from different proportions of glycerol, acylacrylic acid, and other monocarboxylic acid have been established by simple testing, it is possible to prepare, by appropriate selection of proportions, a glycerol mixed ester having any desired degree of improvement in film-forming properties (up to the maximum possible for the ingredients involved) as compared to the glycerol simple ester of the acid other than the acylacrylic acid. More specifically, when the other acid is drying or semi-drying oil acids, it is possible, by appropriate selection of proportions, to prepare a mixed glyceride having the desired degree of improvement (up to the maximum possible for the ingredients involved) as compared to the drying or semi-drying oil whose acids are being used.

The desired proportion of acylacrylic acid glyceride is normally obtained by using the calculated amount of an acylacrylic acid or esterifiable derivative. However, an effect which approaches or equals the behaviour of the mixed ester so made can be obtained by preparing a mixed ester of β-acylacrylic glyceride content higher than that desired, and blending it with the drying oil whose acids are being used (or a different oil if desired) in an amount which is calculated to give a mixed ester of the desired acylacrylic acid glyceride content. When the acylacrylic acid glyceride content is high (e.g., above 25%), the blending is preferably carried out at elevated temperature; suitable conditions are, for example, the heating of the two oils, with stirring and in an inert gas atmosphere, for about 0.5 hour at about 200° C. Under these conditions, it is probable that some interchange occurs, since the film-forming properties are usually better than those of cold blends of the two oils.

As has been indicated, the simple esters of this invention can be prepared by reacting glycerol with the acylacrylic acid,

or with an appropriate esterifiable derivative thereof, such as the anhydride, acid halide, or esters of an alcohol more volatile than glycerol. The esterification reaction can be controlled so that one or more of the alcoholic hydroxyls are esterified. The reaction temperature can be varied widely. With an acid halide or anhydride, temperatures in the neighbourhood of 20—100° C. are sufficient to produce esterification. The direct esterification with acid or the ester interchange process are preferably operated at temperatures above 100° C. and below 275° C.

Also as previously indicated, the mixed esters of the present invention can be made by reacting glycerol simultaneously or successively, in any order, with the several monocarboxylic acids or their esterifiable derivatives. Or a glycerol simple ester of either the acylacrylic acid or other acid can be reacted successively with additional glycerol and the remaining acid or acids. In the first, i.e., alcoholysis, step of this latter process, an ester interchange catalyst, such as litharge, sodium hydroxide or sodium alcoholate, is preferably included in a small amount, suitably from 0.01% to 1.0%. The reaction temperature for the alcoholysis can be varied from 150° C. to 300° C., depending on the extent of alcoholysis desired, the nature and amount of catalyst present, and the susceptibility of the ester to gelation.

Solvents and other preparative details should be adjusted to the method chosen, the manner of so doing being apparent to one skilled in the art. When the solution method heretofore discussed is to be used, any inert water-immiscible liquid which dissolves the product is suitable, hydrocarbons being preferable, and the amount can be varied as desired. Suitable specific solvents include toluene, xylene, cymene, amyl benzene, tetrachloroethane, anisol, and cyclohexanone. Aromatic hydrocarbons, chlorinated solvents, ethers, and ketones are suitable in general. A boiling point in the range 40—200° C. is desirable. The process of the invention can also be carried out in the absence of a solvent.

The monofunctional aliphatic monocarboxylic acid or acids other than the acylacrylic acid can be any monofunctional aliphatic monocarboxylic acid, or any mixture of such acids. Specific additional acids that are suitable include perilla oil acids, oiticica oil acids, China wood oil acids, dehydrated castor oil acids, soya bean oil acids, corn oil acids, cottonseed oil acids, coconut oil acids, oleic acid, stearic acid, lauric acid, butyric acid, crotonic acid and sorbic acid. These acids can be saturated or unsaturated; straight or branched chain; and substituted or not by other groups or atoms, such as ether, ketone or halogen, which do not interfere with the esterification reaction.

Any monofunctional acylacrylic acid, as the term is hereinbefore explained, or any esterifiable derivative thereof, can be employed. The acyl group can be that of any monocarboxylic acid, and it can be present on either the α or β carbon. The acid may or may not contain substituent radicals of any kind which do not interfere with the esterification reaction provided, as said, there be no acyl group attached to the β carbon atom and no thienyl group attached to the α or β carbon atoms. Such radicals can be saturated or unsaturated and substituted or not by inert groups, such as ether, ketone, halogen, and sulphide. The following specific acylacrylic acids can be used in place of the acids of the examples with similar results:

β-(2-naphthoyl) acrylic acid, β-(4-methoxybenzoyl) acrylic acid and β-benzoyl-α: β-dimethylacrylic acid (obtainable, respectively, from naphthalene and maleic anhydride, from anisole and maleic anhydride and from benzene and dimethylmaleic anhydride, according to the general method outlined by von Pechmann, Berichte der Deutschen Chemischen Gesellschaft, 1882, Vol. 15, page 885); β-acetylacrylic acid and α-benzoylcrotonic acid (obtainable, respectively, by condensing aldehyde with acetyl acetate in the presence of hydrogen chloride catalyst according to the method of Claisen and Matthews, Liebig's Annalen der Chemie, 1883, vol. 218, page 172); and 4-ketoheptadien-2 : 5-oic acid, α-acetosorbic acid and α-acetoacrylic acid (obtainable, respectively, from the aldehyde of formula $CH_3CH=CH\ CO\ CHO$—itself obtainable by Claisen condensation of acetaldehyde with pyruvic aldehyde—and acetic acid, from crotonic aldehyde and acetoacetic acid and from formaldehyde and acetoacetic acid, all by the general method of Perkin, Journal of the Chemical Society, 1877, Vol. 31, page 408).

In addition to the particular coating compositions of the examples, the present esters can be formulated into any other desired type of paint, varnish, lacquer, or enamel. Thus, they can be blended by conventional methods with other varnish gums, such as copal, kauri, ester gum, oil-soluble phenol-formaldehyde resins, and rosin-extended phenol-formaldehyde resins, such as "Amberols"; with other resins, such as vinyl or urea-formaldehyde types; with cellulose derivatives, such as nitrocellulose, cellulose acetate, cellulose

aceto-propionate, and ethyl cellulose; with auxiliary components of all kinds, such as waxes, solvents, pigments, and plasticizers, as needed and desired; and to particular advantage with fatty oils, especially drying or semi-drying oils, as is explained above.

These compositions can be applied to many kinds of surfaces and materials, for example, wood, metal, paper, linen, silk, cotton, other textiles and regenerated cellulose wrapping foils. Specific manufactures that can be so produced are linoleum, patent leather, linoxyn-type materials, coated copper wire, oiled cloth, oiled silk, printing inks, and sandpaper. The products of the invention can also be made up into moulding compositions and putties. In addition, they can be employed as modifying agents for urea-formaldehyde and phenol-formaldehyde resins.

It will be apparent from the foregoing description that new esters having remarkable properties and a wide utility have been obtained. In particular, these esters are valuable substitutes for the natural drying oils in coating compositions, thereby reducing materially the dependence upon these natural products. The new esters have also many advantageous properties not shared by the natural oils, as, for example, the remarkable ability to form films which do not crystallize, wrinkle, or frost, as do films from the more rapidly drying natural oils, such as China wood oil. Furthermore, it is possible to take any fatty oil, including one that has a low order of drying, and, by substituting a part of the fatty acid making up that oil by an acylacrylic acid, to improve the drying and film properties greatly. The compositions of the present invention are particularly outstanding in that they combine the high film build of the natural drying oils (resulting from the much higher solids content at working viscosities) with the ability of resin-oil varnishes to dry rapidly to hard, tough films.

We are aware of British Specification No. 569,404 which claims a process for the manufacture of polyhydric alcohol mixed esters which comprises reacting a polyhydric alcohol with at least two organic acids or their esterifiable derivatives, one of the acids being an $\alpha\gamma$-diolefinecarboxylic acid and the other a monofunctional monocarboxylic acid of structure but no mention is made therein of the use of an $\alpha\gamma$-diolefine monofunctional monocarboxylic acid having an acyl group attached to the α or β carbon atom as used herein.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The manufacture of glycerol esters of one or more acylacrylic monofunctional monocarboxylic acids as hereinbefore defined and, if desired, one or more monofunctional aliphatic monocarboxylic acids of different structure by the processes hereinbefore set forth.

2. The manufacture claimed in Claim 1 wherein the monofunctional aliphatic monocarboxylic acid comprises the acids of a natural fatty oil.

3. The manufacture claimed in Claim 2 wherein the natural fatty oil is a drying or semi-drying oil, for example, linseed oil.

4. The manufacture of glycerol esters as hereinbefore particularly described and ascertained especially with reference to the foregoing Examples.

5. Glycerol esters whenever obtained by the manufacture claimed in any of the preceding claims or by the obvious chemical equivalent thereof.

6. Coating compositions comprising the glycerol esters claimed in Claim 5.

Dated the 25th day of June, 1943.

E. A. BINGEN,
Solicitor for the Applicants.

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